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Pump-Probe Study of fs-Laser Hyperdoping and Texturing of Silicon for Advanced Non-equilibrium Materials

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Final Report

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In this final report, we describe our progress in studying ultrafast laser modification of silicon, with a focus on better understanding the inception of surface texturing and laser-indcued periodic surface structures (LIPSS) at low fluences. We also briefly describe the recent extension of our work to ultrafast laser modification of gallium phosphide (GaP), a III-V semiconductor material with high second-order nonlinear susceptibility. We close with a discussion of other current work, including fundamental studies of nanosecond-laser treatment of germanium (Ge) in order to develop hyperdoped Ge for Short Wavelength-Infrared (SWIR) photodetection, future directions, and a list of published work supported thus far through the AFOSR's support. We sincerely thank the AFOSR for its continued support throughout the project.

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Pump-Probe Study of fs-Laser Hyperdoping and Texturing of Silicon for Advanced Non-equilibrium Materials

AFOSR Final Report (end date 31 May 2017)

PI: Eric Mazur, Harvard University
Program Manager: Dr. Enrique Parra, Ultrashort Pulse Laser-Matter Interactions

Abstract

In this final report, we describe our progress in studying ultrafast laser modification of silicon, with a focus on better understanding the inception of surface texturing and laser-indcued periodic surface structures (LIPSS) at low fluences. We also briefly describe the recent extension of our work to ultrafast laser modification of gallium phosphide (GaP), a III-V semiconductor material with high second-order nonlinear susceptibility. We close with a discussion of other current work, including fundamental studies of nanosecond-laser treatment of germanium (Ge) in order to develop hyperdoped Ge for Short Wavelength-Infrared (SWIR) photodetection, future directions, and a list of published work supported thus far through the AFOSR's support. We sincerely thank the AFOSR for its continued support throughout the project.

1) Ultrafast laser modification of Silicon

First, we start with continued research progress over the past year, including understanding the irradiation conditions required for ultrafast laser texturing of silicon using stationary pulses with a focus on initial surface textures. We studied the initial formation of surface textures at low fluences. We observed that the initial modification of the surface consists of randomly distributed areas that range in size from sub-micrometer to around ten micrometers. Within these modified areas, surface ripples are formed in the direction of (or orthogonal to) the laser electric field polarization direction, indicating that surface plasmon polaritons form the ripples. Within some of these modified areas, the surface ripples grow rapidly in the direction of the electric field polarization, as shown in Figure 1. These results are available in (Franta, 2016).

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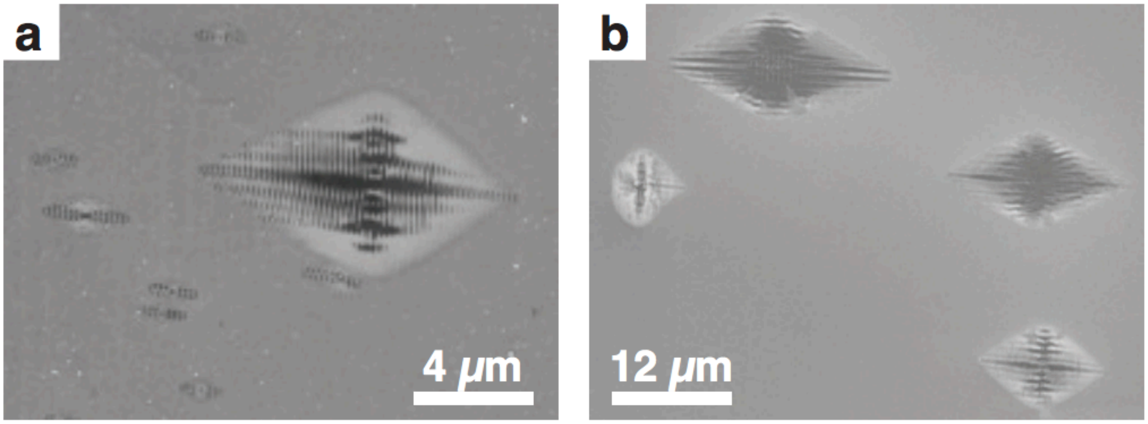

Figure 1: Initiation of surface textures on Si after ultrafast laser irradiation. Randomly distributed areas of surface modification (a and b) contain surface ripples that grow in the direction of the laser electric field polarization. 1.5 kJ/m^2 pulses in 20 Torr N_2 with a) 110 pulses and b) 150 pulses. Pulse duration 80 fs.

2) Ultrafast laser modification of III-V Semicondcutors

Over the last months of the project, we extended our findings to new material systems, namely III-V semiconductors. Unlike Si, there have been very little explorations on ultrafast laser nanostructuring and formation of LIPSS on III-V semiconductors. Therefore, applying LIPSS to III-Vs can enrich this untouched territory and would bring new functionalities and applications to the existing ones. Moreover, the possibility to simultaneously modify the material properties (e.g., periodic change of refractive index and induced optical anisotropy), is a big advantage over other nanofabrication methods (e.g., top down approach). This can be very promising for many photonic applications including nonlinear optics.

Amongst semiconductor materials, zincblende GaP (III-V semiconductor) which belongs to the $\bar{4}3m$ space group, with its high second order nonlinear coefficient (159 pm/V at λ=852 nm) broad transparency range (~ 0.5-11 μm), and high thermal conductivity (110 W/mK) is an excellent candidate for many photonic applications. GaP has an indirect band gap of 2.26 eV, transparent at 800 nm, and also has a very high second-order optical nonlinearity (159 pm/V). Our preliminary results show formation of HSFL (Figure 2) with period of 180 nm, which is about λ/2n, where n is the refractive index of the sample, and λ the laser wavelength, when irradiated with femtosecond laser pulses at 800 nm below the melting threshold. By testing the effect of fluence and polarization of the fs-laser on the formation of HSFL, we also aim to better understand the mechanism behind the ultrafast laser-matter interaction in GaP in this regime.

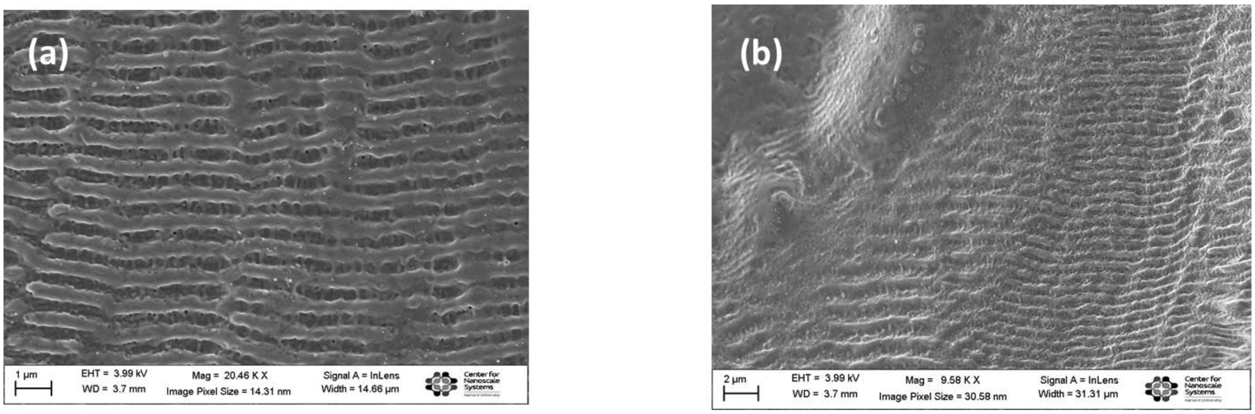

Figure 2: LIPSS formation in GaP (1 0 0), at λ=800 nm, 100 fs duration, 1 kHz repletion rate, and a fluence of 0.5 J/cm^2. **(a)** High spatial frequency LIPSS formation after 20 pulses. **(b)** high and low spatial frequency LIPSS in the center and periphery of the beam, respectively after 150 pulses.

3) Hyperdoping Germanium

In addition to the above works on studying the ultrafast laser modification of semiconductors (Si and GaP), we have recently worked on hyperdoping germanium using ion implantation and nanosecond pulsed laser melting. We so far filed two provisional patents on this work, submitted one publication, and are currently writing two more publications on this work.

In this hyperdoping process, ion implantation allows a non-equilibrium concentration of dopants to be inserted into the germanium lattice with control over the dopant dose and depth profile. Nanosecond pulsed laser melting heals the implantation damage and achieves non-equilibrium concentrations several orders of magnitude above the solid solubility limit in a crystalline structure through the process of solute trapping. In solute trapping, the re-solidification front advances slowly enough for epitaxial regrowth to occur from the underlying crystalline substrate seed, but fast enough to prevent dopant atoms from diffusing away from the melt front towards the interface.

Preliminary results of prototype hyperdoped germanium demonstrate its game-changing potential for Short Wavelength-Infrared (SWIR) (1–3µm) photodetection (Fig. 3). SWIR (1–3µm) photodetection is increasingly important for a range of exciting applications: industrial and medical imaging, agricultural inspection, LiDAR, chemical and biological sensing, and surveillance. Hyperdoped germanium represent a fundamentally different type of material platform for SWIR photodetection than current SWIR materials. Hyperdoped germanium-on-silicon photodetectors absorb and detect sub-band-gap SWIR light through dopant-mediated, extrinsic photoconductivity. Initial results of prototype hyperdoped germanium demonstrate that it is perfectly single-crystal and hyperdoped (Ge:Au, approximately 0.2 at. %, five orders of magnitude beyond the Ge:Au equilibrium solubility limit).

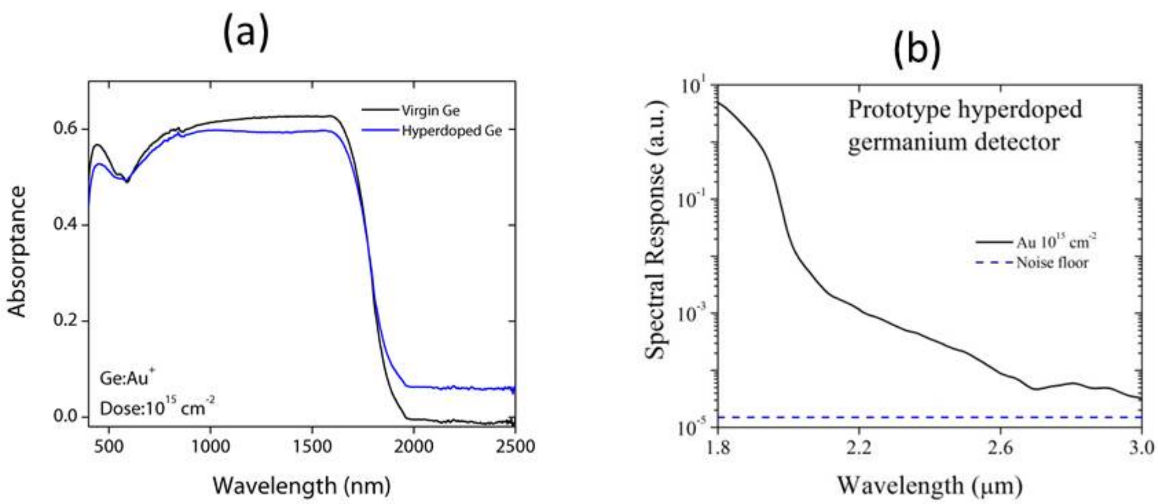

Figure 3: (a) The optical absorptance of a hyperdoped germanium wafer (70-nm, 0.2 atomic % Ge:Au layer) relative to a virgin Ge wafer. With fabrication optimization, the hyperdoped layer thickness can be extended to at least 500nm to increase sub-band-gap absorptance. **(b)**Room temperature optoelectronic response of a prototype photodiode made from hyperdoped germanium. The photodiode was illuminated with a globar source and its spectral response was measured using a Fourier transform infrared spectrometer. The measured optoelectronic response above the noise floor extends to at least 3 µm

Moving forward we plan to systematically study the properties of hyperdoped germanium to evaluate its full-potential as a paradigm shifting photodetector material for societally important SWIR applications.

Recent publications

- Benjamin Franta, Eric Mazur, S.K. Sundaram. "Ultrafast laser processing of silicon for photovoltaics" *International Materials Reviews*. Nov 2017

- David Pastor‡*, **Hemi H. Gandhi‡***, Corentin P. Monmeyran, Austin J. Akey, Ruggero Milazzo, Yan Cai, Enrico Napolitani, Russell M. Gwilliam, Iain F. Crowe, L. C. Kimerling*, Jurgen Michel, Anuradha Agarwal, Eric Mazur, and Michael J. Aziz*. "High Active N Type Doping of Strained Germanium Though Co-Implantation and Nanosecond Pulsed Laser Melting," *Submitted To Journal Of Applied Physics October 2017*

- Hemi H. Gandhi‡*, David Pastor‡*, Tuan T. Tran, Lachlan A. Smillie, Austin J. Akey, Ruggero Milazzo, Enrico Napolitani, J.S. Williams, Michael J. Aziz*, Eric Mazur*. "Hyperdoped Germanium Photodetectors With Room Temperature Sub-Gap Optoelectronic Response To 3um," *Manuscript In Preparation, To Be Submitted*

- Hemi H. Gandhi‡*, David Pastor‡*, Tuan T. Tran, Lachlan A. Smillie, Austin J. Akey, Ruggero Milazzo, Enrico Napolitani, J.S. Williams, Michael J. Aziz*, Eric Mazur*. "Chalcogen Hyperdoped Germanium Photodiodes Photodetectors With Room Temperature Sub-Gap Optoelectronic Response," *Manuscript In Preparation, To Be Submitted*

- Franta, B. (2016). Fabrication techniques for femtosecond laser textured and hyperdoped silicon. PhD, Harvard University.

PROVISIONAL PATENTS

- "N-TYPE DOPING OF STRAINED EPITAXIAL GERMANIUM FILMS THROUGH CO-IMPLANTATION AND NANOSECOND PULSED LASER MELTING", Hemi H. Gandhi, David Pastor, Michael J. Aziz, Eric Mazur, *Filed Nov 2016 Through Harvard University Office Of Technology and Development and Pepper Hamilton LLP*

- "HYPERDOPED GERMANIUM-BASED PHOTODIODES WITH SUB-BAND GAP PHOTORESPONSE AT ROOM TEMPERATURE," *Hemi H. Gandhi, David Pastor, Eric Mazur, Michael J. Aziz, Filed March 2017 Through Harvard University Office Of Technology and Development and Pepper Hamilton LLP*